

Equilibrium swelling and universal ratios in dilute polymer solutions: Exact Brownian dynamics simulations for a delta function excluded volume potential

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A narrow Gaussian excluded volume potential, which tends to a δ -function repulsive potential in the limit of a *width* parameter d^* going to zero, has been used to examine the universal consequences of excluded volume interactions on the equilibrium and linear viscoelastic properties of dilute polymer solutions. Brownian dynamics simulations data, acquired for chains of finite length, has been extrapolated to the limit of infinite chain length to obtain model independent predictions. The success of the method in predicting well known aspects of static solution properties suggests that it can be used as a systematic means by which the influence of solvent quality on both equilibrium and non-equilibrium properties can be studied.

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There is a growing recognition of the importance of solvent quality in determining the rheological properties of dilute polymer solutions. Though there are relatively few systematic experimental investigations of the influence of solvent quality, nevertheless there is sufficient evidence that material functions, in both shear and extensional flows, are significantly different from each other in good and θ -solvents [1, 2, 3]. While the theoretical description of the influence of solvent quality on the *equilibrium* behavior of dilute polymer solutions has been a major area of research [4], the description of its influence on *non-equilibrium* behavior is still in its infancy. Most current non-equilibrium theories do not attempt to develop a unified framework that is also applicable at equilibrium, and the wealth of experience and insight that has been gained so far in the development of static theories is rarely used in the description of dynamic behavior. In this paper, we introduce an approach that provides a consistent means of describing both regimes of behavior, and as a first step towards establishing the usefulness of the methodology, we demonstrate that the method is capable of reproducing well known universal static results. We also show that, even in the case of well established results, the method is capable of providing new and additional insights. Furthermore, as an example of the versatility of the approach, the influence of solvent quality on a universal ratio of *linear viscoelastic* properties, is reported here for the first time.

One of the most important results of the experimental investigation of the static behavior of dilute polymer solutions, has been the discovery that various properties—both in θ -solvents and in good solvents—exhibit power law behavior when the molecular weight of the dissolved polymer is sufficiently large. It is perhaps less commonly known that even when the molecular weight is not very large, a type of scaling still persists, which enables the description of behavior with the help of a single parameter. An illustrative example is the behavior of the root mean square radius of gyration, R_g . Light scat-

tering measurements indicate that for molecules of sufficiently large molecular weight M , R_g obeys the power law $R_g = aM^\nu$, where the pre-factor a depends on the particular polymer-solvent system, but the exponent ν does not. In a θ -solvent, the *universal* exponent has a value, $\nu = 0.5$, while in a good solvent, $\nu = 0.592 \pm 0.003$ [5]. A remarkable experimental observation is that, away from the large molecular weight asymptotic limit, the dependence of the mean size of the polymer molecule on both the temperature, T , of the solution and M , can be combined into a single variable, $\tau(T)\sqrt{M}$, where, $\tau(T)$ is a simple function of temperature, $\tau = (1 - T_\theta/T)$, with T_θ denoting the θ -temperature. A vast amount of equilibrium data for a variety of polymer solvent systems reveals that, when the *swelling* α_g of a polymer molecule—defined as the ratio of the radius of gyration in a good solvent to the radius of gyration in a θ -solvent—is plotted as a function of $\tau\sqrt{M}$ (with each polymer-solvent system being shifted horizontally by a suitable constant factor), universal behavior is displayed, for all values of the molecular weight M , and temperature $T > T_\theta$ [5, 6, 7].

The entire range of behavior exhibited by static solution properties has been successfully predicted by applying renormalization group (RG) methods [4]. In these theories, the macromolecule is frequently represented by a *coarse-grained* model, such as a bead-spring chain, consisting of N beads connected together by $(N-1)$ *Hookean* springs (with a spring constant H). The presence of excluded volume interactions is then taken into account by assuming the existence of a Dirac delta function repulsive potential, that acts pairwise between the beads of the chain [8],

$$E(\mathbf{r}_{\nu\mu}) = v(T) k_B T \delta(\mathbf{r}_{\nu\mu}) \quad (1)$$

where, $v(T)$ is the excluded volume parameter, k_B is Boltzmann's constant, and $\mathbf{r}_{\nu\mu}$ is the vector connecting beads ν and μ . In the limit $T \rightarrow T_\theta$, it can be shown that v depends on T through the relation, $v(T) = v_0 \tau(T)$, where v_0 is a constant [8]. If a length scale, $\ell =$

$\sqrt{k_B T/H}$, and a non-dimensional *strength* of excluded volume interactions, $z^* = v(2\pi\ell^2)^{-3/2}$ are defined, then both the temperature and the chain length dependence can be combined into the single non-dimensional parameter, $z = z^*\sqrt{N}$. Completely consistent with experimental observations (since $z \propto \tau\sqrt{M}$), RG theories predict the existence of power laws in the limit $z \rightarrow 0$ (corresponding to θ -solvents), and the excluded volume limit $z \rightarrow \infty$ (corresponding to good solvents), and the existence of *scaling functions*, that depend only on the parameter z , which accurately describe the crossover behavior between these two asymptotic limits [4].

In spite of the success of RG theories, it must be borne in mind that they are approximate theories, dependent to some extent on the order of the original perturbation calculation on which they are based. Exact numerical results for the excluded volume problem can, on the other hand, be obtained by either Monte Carlo simulations of self avoiding walks on lattices [9, 10], or by off-lattice Monte Carlo simulations [11]. Since δ -functions cannot be used in numerical investigations, off-lattice Monte Carlo simulations are typically based on excluded volume potentials with a finite range of excluded volume interactions, such as the Lennard-Jones potential. An important point to be noted, however, is that the parameter z , which is the true measure of solvent quality, does not appear naturally when potentials like the Lennard-Jones potentials are used. Instead, simulation results are functions of the parameters that characterize the potential. It is possible, however, to infer the value of z from simulation results by carrying out a data shifting procedure similar to that used to bring experimental data onto a universal curve, i.e, data for various values of chain length N , and various distances from the θ -temperature, can be brought to lie on a master curve [11]. The procedure is quite involved and even the θ -temperature must first be estimated from simulations. Furthermore, Monte Carlo methods cannot be used to estimate rheological properties in general flow fields, and so it is not clear how this procedure can be extended to systematically examine the influence of solvent quality on non-equilibrium properties.

The self-similar character of polymer molecules, which is responsible for the universal behavior exhibited by polymer solutions at equilibrium, is also responsible for the universal behavior displayed away from equilibrium [8]. An important and fundamental challenge for molecular theories is to verify the existence of this universal behavior. The universal consequences of excluded volume effects away from equilibrium has been examined by Öttinger and co-workers [12, 13] with the help of RG methods. Since these methods lead to approximate predictions, it is important to be able to assess their accuracy. Further, these papers were focussed on predicting the universal behavior in the excluded volume limit,

and cross-over scaling functions for rheological properties were not reported.

In this paper, we introduce a procedure by which universal cross-over scaling functions and asymptotic behavior in the excluded volume limit can be obtained for a δ -function excluded volume potential, both at equilibrium and away from it. In other words, a means has been obtained by which an *exact* numerical solution to the Edwards model, which is of fundamental importance to polymer physics, can be found. Using the suggested methodology, provided sufficient computational time is used, properties predicted by the Edwards model can be found to a high degree of accuracy. As a result, the influence of solvent quality, measured directly in terms of the parameter z , can be systematically examined, and results obtained by approximate RG calculations may be verified.

A detailed discussion of the theoretical framework used here may be found in earlier papers by Prakash [14, 15]. Essentially, macroscopic properties are obtained by exploiting the mathematical equivalence of diffusion equations in polymer configuration space and stochastic differential equations for the polymer configuration. Since averages calculated from stochastic trajectories are identical to averages calculated from distribution functions, stochastic trajectories are generated by numerically integrating the appropriate stochastic differential equation with the help of Brownian dynamics simulations (BDS) [16].

A key ingredient in our approach is the use of a narrow Gaussian potential (NGP),

$$E(\mathbf{r}_{\nu\mu}) = \left(\frac{z^*}{d^{*3}}\right) k_B T \exp\left\{-\frac{H}{2k_B T} \frac{\mathbf{r}_{\nu\mu}^2}{d^{*2}}\right\} \quad (2)$$

where, d^* is an additional non-dimensional parameter that measures the range of excluded volume interaction. The NGP is a means of regularizing the δ -function potential since it reduces to the δ -potential in the limit of $d^* \rightarrow 0$. The central hypothesis behind the use of this potential is that when data accumulated for chains of finite length is extrapolated to the infinite chain length limit, universal consequences of the presence of excluded volume interactions will be revealed, independent of the value of d^* . Initial attempts to carry out this program were unsuccessful because of the computational intensity of BDS. The essential soundness of the procedure has, however, been established by obtaining universal predictions, both at equilibrium and in the linear viscoelastic limit [17], and at finite shear rates in steady simple shear flow [15], with an approximate version of the theory—the so called *Gaussian approximation*. The parameter d^* has been shown to be irrelevant in the long chain limit, since it always appears in the theory as the ratio d^*/\sqrt{N} .

An exact numerical solution of the model has been obtained in this work, and the computational difficulties

encountered earlier have been overcome, by adopting two new strategies (apart from the obvious one of parallelizing the code). First, a novel trajectory in the (d^*, z^*) parameter space has been used to reach the asymptotic limit. Second, a variance reduction procedure based on the method of control variates [16], with the Rouse model as the control variate, has been implemented. While these strategies, which are discussed in greater detail elsewhere [18], do not alter the scaling of CPU time with N (which continues to increase roughly as N^3), they ensure that the noise is sufficiently small to permit an accurate extrapolation of finite chain data, even for fairly small chains.

Two different approaches have been adopted here to obtain results in the limit $N \rightarrow \infty$. In the first, z is kept constant while simulations are carried out with increasing values of N . Extrapolation of the accumulated data to $N \rightarrow \infty$ implies the simultaneous limit, $z^* \rightarrow 0$ (or equivalently, $T \rightarrow T_\theta$). As a result, crossover functions for systems close to the θ -temperature are obtained. In the second approach, z^* is maintained constant (which is equivalent to T being constant) while N is increased systematically. Extrapolation to $N \rightarrow \infty$ in this case leads to the prediction of behavior in the excluded volume limit, $z \rightarrow \infty$.

The crossover scaling function for the swelling α_g^2 , as a function of z , is displayed in Fig. 1(a). The experimental data of Miyaki and Fujita [6] for polystyrene of various molecular weights and temperatures has been shifted to lie on the simulation data, using a single constant horizontal shift factor for each of the two solvents [18]. The remarkable agreement of the predicted equilibrium swelling with experimental data, similar to that obtained earlier by RG theory [4], has been obtained by using bead-spring chains with a maximum of just 36 beads. The BDS data has been curve-fitted with an equation commonly used to fit results of RG analysis [4], $\alpha_g^2 = (1 + az + bz^2 + cz^3)^{(4\nu-2)/3}$, with the coefficient a kept fixed at its first order perturbation value [4]. It leads to the prediction $\nu = 0.6004 \pm 0.0004$, which is about 2% greater than the value $\nu = 0.588$ predicted by RG theory. The maximum difference between the computed data and the curve fit was less than 0.6%. As shown below, we find that ν estimated in the excluded volume limit, with the present procedure, is also about 2% more than 0.588.

The efficacy of the present approach is demonstrated in Fig. 1(b), where the crossover behavior of the universal ratio constructed from the zero shear rate first normal stress difference coefficient and the zero shear rate viscosity, $U_{\Psi\eta} = n_p k_B T \Psi_{1,0} / \eta_{p,0}^2$ (with n_p denoting the number density of polymers), is displayed. To our knowledge, this crossover behavior has not been reported elsewhere before. The only existing universal prediction is a RG calculation in the excluded volume limit (indicated

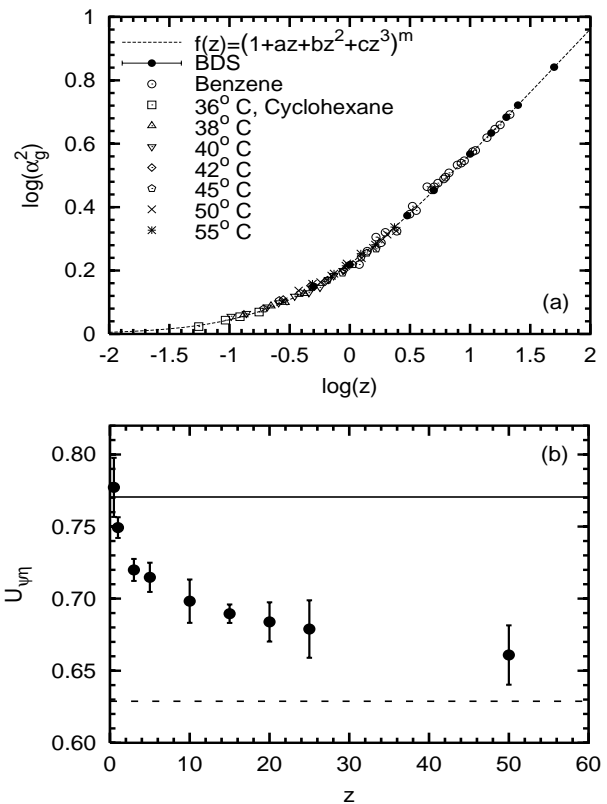


FIG. 1: Crossover scaling functions. (a) Swelling of the radius of gyration, α_g^2 , versus the strength of excluded volume interaction, $z = z^*(T)\sqrt{N}$. Experimental data for polystyrene in the two solvents is that of Miyaki and Fujita [6]. (b) Universal ratio $U_{\Psi\eta}$ as a function of z . The solid line is the prediction in the excluded volume limit, while the dashed line is the prediction of RG theory.

in the figure by the dashed line), obtained by refining a first order perturbation expansion [12].

In the Rouse model, $U_{\Psi\eta} = \text{constant} = 0.8$. It is also expected to be constant, independent of the polymer-solvent system, in the excluded volume limit. The figure suggests that the crossover function approaches the value predicted by RG theory, $U_{\Psi\eta} = 0.6288$, as $z \rightarrow \infty$. On the other hand, as indicated by the solid line, a significantly different value of $U_{\Psi\eta} = 0.77 \pm 0.01$ is predicted by the present approach in the excluded volume limit. It is of interest to see if a RG calculation based on a higher order perturbation theory would lead to a prediction in agreement with the present prediction. A similar difference, between the large z limit suggested by the crossover behavior, and the value obtained in the excluded volume limit, has been observed previously in the case of the universal ratio $U_R = \alpha_g^2 / \alpha_e^2$, where α_e^2 is the swelling of the end-to-end vector. The behavior of U_R predicted by the present approach will be discussed elsewhere [18].

Although the scaling of R_g with chain length N obeys a power law only in the limit of long chains, one can

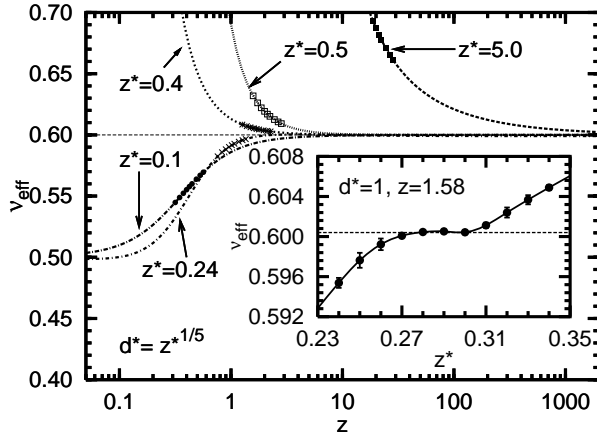


FIG. 2: The exponent ν_{eff} , in the expression $R_g \sim N^{\nu_{\text{eff}}}$, as a function of z , and in the inset, as a function z^* .

make the ansatz, $R_g \sim N^{\nu_{\text{eff}}}$, with ν_{eff} representing an effective exponent that approaches its critical value as $N \rightarrow \infty$. By carrying out high precision Monte Carlo studies of lattice self avoiding walks, Sokal and co-workers [9] have observed that ν_{eff} approaches its asymptotic value *from above*, in contrast to modern two-parameter theories for the continuum Edwards model that predict that the asymptotic value is reached *from below*. This has prompted them to suggest that these theories do not correspond to good solvents in general, but instead to an infinitesimal region just above the theta temperature. Schäfer and co-workers [4, 10] have shown, by developing an alternative renormalization group method, and by Monte Carlo simulations, that both approaches to the asymptotic limit are not incompatible due to the existence of a two branched structure to the solution of the excluded volume problem. Their results indicate that the excluded volume limit is approached on two distinct branches, depending on the whether $z^* < z_f^*$ (the weak-coupling branch), or $z^* > z_f^*$ (the strong-coupling branch), where z_f^* denotes the *fixed point* for the parameter z^* . While the existence of a dual branched structure has only recently been elucidated, the various curves in Fig. 2, for ν_{eff} as a function of z , show that Brownian dynamics simulations readily reveal the presence of this structure. Indeed, as will be discussed below, a unique way can be developed by which the distinctive structure of the solution may be exploited to find both the fixed point and the critical exponent. The curves in Fig. 2 have been obtained (i) by fitting α_g^2 versus z data, for $z^* < z_f^*$, with $\alpha_g^2 = (1 + az + bz^2)^{2\nu-1}$; (ii) by fitting the data for $z^* > z_f^*$ with $\alpha_g^2 = az^{4\nu-2} [1 - bz^{-|m|} (1 + c/z^{-|1+m|})]$; and (iii) by using the fact that $\nu_{\text{eff}} = 0.5 + 0.25(\partial \ln \alpha_g^2 / \partial \ln z)$. In both the curve-fitting expressions used for parameterizing the data (whose forms have been suggested earlier by Grassberger et al. [10]), the value of ν has been set

equal to 0.6.

On the weak-coupling branch (strong-coupling branch), ν_{eff} first increases (decreases) rapidly before approaching the asymptotic value very gradually. We consequently expect a plot of ν_{eff} vs z^* , for constant values of d^* and z , to show a point of inflection at the fixed point. This is clearly seen in the inset of Fig. 2, which describes the change in ν_{eff} as a function of z^* , for a range of values of z^* spanning the fixed point. The figure suggests that the fixed point lies in the range $0.28 \leq z_f^* \leq 0.3$, and that the value of ν_{eff} in this range is 0.6004 ± 0.0002 , which is expected to be close to the critical value, since asymptotic behavior is attained at relatively small values of N as $z^* \rightarrow z_f^*$. Schäfer and co-workers [4, 10] have estimated $z_f^* = 0.364$, while recently Prakash [15] has shown in the Gaussian approximation that, $z_f^* \approx 0.35$. It is an exciting prospect to see if this two branched structure persists into the non-equilibrium regime—an issue that is easily examinable within the framework introduced in this work.

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- [1] I. Noda, Y. Yamada, and M. Nagasawa, *J. Phys. Chem.* **72**, 2890 (1968).
- [2] M. J. Solomon and S. J. Muller, *J. Rheol.* **40**, 837 (1996).
- [3] T. Sridhar, D. A. Nguyen, and G. G. Fuller, *J. Non-Newtonian Fluid Mech.* **90**, 299 (2000).
- [4] L. Schäfer, *Excluded Volume Effects in Polymer Solutions* (Springer-Verlag, Berlin, 1999).
- [5] R. C. Hayward and W. W. Graessley, *Macromolecules* **32**, 3502 (1999).
- [6] Y. Miyaki and H. Fujita, *Macromolecules* **14**, 742 (1981).
- [7] M. Bercea, C. Ioan, S. Ioan, B. C. Simionescu, and C. I. Simionescu, *Prog. Polym. Sci.* **24**, 379 (1999).
- [8] M. Doi and S. F. Edwards, *The Theory of Polymer Dynamics* (Oxford University Press, Oxford, 1986).
- [9] B. Li, N. Madras, and A. D. Sokal, *J. Stat. Phys.* **80**, 661 (1995).
- [10] P. Grassberger, P. Sutter, and L. Schäfer, *J. Phys. A: Math. Gen.* **30**, 7039 (1997).
- [11] W. W. Graessley, R. C. Hayward, and G. S. Grest, *Macromolecules* **32**, 3510 (1999).
- [12] H. C. Öttinger, *Phys. Rev. A* **40**, 2664 (1989).
- [13] W. Zylka and H. C. Öttinger, *Macromolecules* **24**, 484 (1991).
- [14] J. R. Prakash, *Macromolecules* **34**, 3396 (2001).
- [15] J. R. Prakash, *J. Rheol.* **46**, 1353 (2002).
- [16] H. C. Öttinger, *Stochastic Processes in Polymeric Fluids* (Springer-Verlag, 1996).
- [17] J. R. Prakash, *Chem. Eng. Sci.* **56**, 5555 (2001).
- [18] K. S. Kumar and J. R. Prakash, to be published.